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Removal of hormones and antibiotics by nanofiltration membranes

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Abstract

The removal of several hormones and antibiotics by nanofiltration membranes was studied in mixed solutions. The effects of solution chemistry, organic matter and salinity were investigated on the rejection of tetracycline's and sulfanamides and selected hormones and their adsorption on membranes. Tetracyclines were observed to have a high adsorptive affinity for the membrane. Almost 80% of chlorotetracycline was adsorbed on the membrane surface compared with 50% for doxcycline while the adsorption rates for hormones were lower than those obtained for tetracyclines. Addition of calcium, organic matter and salinity had an influence on the rejections. Rejection of sulfanamides was low compared to hormones and tetracyclines. Addition of antibiotics to hormone solution increased the hormone rejections while almost complete rejections were observed for tetracyclines.

Keywords: Nanofiltration; Hormone; Antibiotics; Adsorption

1. Introduction

There is a growing awareness of the importance of trace levels of organic compounds as contaminants originating from industrial, agricultural, medical and domestic uses. Compounds used in personal care products, pharmaceuticals and other consumables as well as hormones may enter aquatic environments after passing through wastewater treatment plants, which often are not designed to remove these chemicals [1,2]. In addition, veterinary pharmaceuticals and growth promoters used in animal husbandry may be released directly to the environment with animal wastes through overflow or leakage from storage facilities or land application [1,3].

As early as 1973, Norpoth et al. [4] indicated that the use of contraceptives may cause severe long-term problems due to the high persistence and biological activity of those compounds in the environment. Evidence now exists that hormones and pharmaceuticals are widespread in effluents of sewage treatment plants [5]. One of the first results concerning environmental occurrence of pharmaceuticals was reported by several researchers [6–8] who detected clofibric acid in treated sewage in the US. Further studies were obtained in Great Britain [9] and Canada [10]. However, extensive investigation of the occurrence of hormones and pharmaceuticals in the environment began in the 1990s, when the first analytical methods were developed allowing for the determination of pharmaceuticals in aqueous matrices [11].

Many scientific reports have documented the environmental and health implications of hormones and antibiotics. Although, the concentrations of hormones and antibiotics in drinking water and wastewaters are at low levels (ng/l), these compounds may accumulate in animals. Several studies have suggested a link between environmental exposures to hormones and deteriorating trends in human health including decreases in male sperm count; increase in testicular, prostate, ovarian and breast cancer; and reproductive malfunctions [12–17]. Desbrow et al. [18] found levels of hormones in domestic effluent samples at concentrations up to 80 ng/l. A recent study conducted by the US Geological Survey on fresh water resources that receive effluents from across the US showed the occurrence of estradiol and estrone in approximately 7–10% of the water samples with maximum concentrations up to 93 and 112 ng/l, respectively [1]. Estradiol concentrations ranging from 6 to 66 ng/l have been found in ground water [19] and in the South Nevada water sys-

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tem at 2.6 μg/l [20,21]. More than 70 different pharmaceutically active compounds have been detected at concentrations up to the μg/l level in sewage effluents, surface waters, groundwater and drinking water [22]. Recent studies showed that tetracycline as high as 4 μg/l and chlorotetracycline at 1.2 μg/l have been detected in municipal wastewater [23,24]. According to a study obtained in 144 different water samples collected between April 1999 and April 2001 [25], tetracyclines and sulfanamides were detected in samples from 9 sites (6% detections) in concentrations ranging from 0.07 to 15 μg/l. The majority of these detections were from surface water sites. Only one site had detection in groundwater. This sample was a groundwater site from Washington and contained the sulfamethaxazole. Overall, 7 of the 144 groundwater and surface water sites were found to contain sulfanamides and six sites were found to contain tetracyclines. Chlortetracycline was detected at 0.15 μg/l in one surface water sample, and the most commonly detected tetracycline was oxytetracycline.

The occurrence of these materials in natural waters has led to a search for treatment methods to remove hormones and antibiotics. This concern is particularly critical for water reuse applications where there is a potential for concentration of these contaminants in the course of repeated water recycling. Coagulation alone is generally not effective in removing these trace-level organic compounds. However, activated carbon adsorption, advanced oxidation and membrane filtration can effectively remove trace organic compounds [8]. Oxidation of EDCs and pharmaceuticals can result in reaction and transformation of these compounds [25]. Removal of tetracyclines was investigated using activated sludge at different sludge and hydraulic retention times and removal efficiencies of 80–85% were obtained [23].

Membrane filtration using nanofiltration (NF) and reverse osmosis (RO) membranes is one of the most promising techniques for the removal of hormones [21] and antibiotics [26–29]. However, there are few data available on the rejection of these chemicals by NF and RO membranes, particularly under conditions present in wastewater treatment plant systems where there may be multiple species interacting in solution and on the membrane surfaces. There is some indication that interaction with naturally occurring solutes such as natural organic matter may enhance the removal efficiency of NF and RO membranes [30–32].

During the early stages of membrane filtration, adsorption on the membrane may play an important role in reducing the concentration of hormones that move across the membrane. However, after the adsorption capacity has been saturated, the apparent removal efficiency may decrease due to the partitioning and subsequent diffusion of the hormones [21]. Adams et al. [27] evaluated the conventional drinking water treatment processes including RO to determine their effectiveness in the removal of seven common antibiotics. In these experiments, reverse osmosis was shown to be effective in removing all of the studied compounds. Drewes et al. [33], investigated the different treatment technologies (activated sludge, tricking filter, NF and RO) for removing pharmaceuticals at full scale facilities. None of the drugs investigated was detected in tertiary treated effluents after NF and RO. Ngheim et al. [29] investigated the removal of sulfanamides by NF membranes and determined that retention of pharmaceuticals by a tight NF membrane is dominated by size exclusion, whereas both electrostatic repulsion and size exclusion govern the retention by loose NF membranes.

The objective of this study is to elucidate the removal mechanism of antibiotics and hormones by NF membranes in mixed solutions. The effects of solution chemistry, organic matter and salinity were investigated. In addition, the interactive effects of hormones on antibiotic removal and antibiotics on hormones removal were also investigated.

2. Materials and methods

2.1. Experimental set-up

Experimental procedures used in this work have been previously described [34] and are summarized here. Experiments were performed using a dead-end filtration cell. The dead-end filtration (DEF) set-up consisted of a 300 ml stirred cell (Sterlitech, HP4750) pressurized with air. The active membrane area of the DEF cell was 14.6 cm^2 and a sample volume of 200 ml was used in each experiment. Permeate flux was determined by weight using a Scientech 5200 model electronic balance and the results sent to computer by data logging system. The DEF unit was stirred with a magnetic stirrer (Thermolyne Cimarec, model no: S46415) at a constant speed of 200 rpm. In all cases, experiments were performed at room temperature of 20 ± 1 °C.

Prior to each experiment, membranes were compacted for approximately 1 h by passing ultra pure water through the system until a constant permeate flux (initial clean water flux) was achieved. A 200 ml volume of the test water was then added to the DEF cell and filtration of the sample was carried out at 10 bar (145 psi), until more than 85% of the volume had passed through the membrane, in a batch mode. After each run, the membrane was replaced with a new membrane.

2.2. Membrane

Filtration experiments were performed using the nanofiltration membrane (NF200) (Film Tech Corp., Minneapolis, MN). The molecular weight cut off for this NF membrane is reported by the manufacturer to be between 200 and 300 Da. Results from contact angle measurements indicated that the NF membrane had a hydrophilic surface with a contact angle of 25°. NF200 membrane is highly negatively charged at pH 7.0, with the zeta potential of about −19 mV and IEP of around 4.6 [35]. Membrane sheets were cut into smaller pieces in order to fit the dead end cells with 14.6 cm^2 of active membrane area [31].

3. Water matrix and chemicals

Synthetic solutions were prepared for the experiments. Antibiotics and hormones were mixed with 10 mM calcium chloride, 10 mg/l humic acid, and 10 mM NaCl. In addition

Table 1
List of chemicals and characteristics [36]

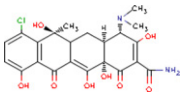
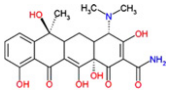
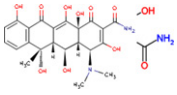
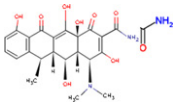
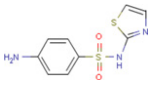
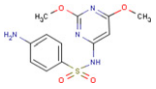
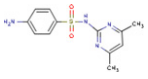
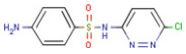
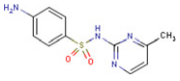
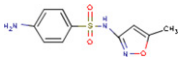
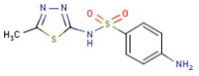
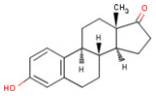
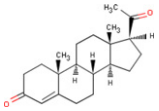
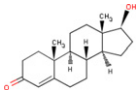
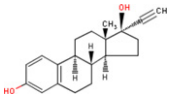
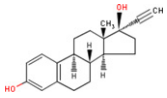
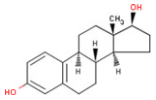
Chemicals	Name	Molecular formula	Molecular weight (g/mol)	p*Ka*	Solubility in water (mg/l)	log P_{ow}	Structure
Tetracyclines	Chlorotetracycline [25]	$C_{22}H_{23}N_2O_8Cl_1$	479	3.3	630	−0.62	
	Tetracycline [25]	$C_{22}H_{24}N_2O_8$	444.44	3.3	231	−1.3	
	Oxytetracycline [25]	$C_{22}H_{24}N_2O_9$	460.44	3.27	313	−0.9	
	Doxcycline [25]	$C_{22}H_{24}N_2O_8$	444.44		630	−0.02	
Sulfanamides	Sulfathiazole [25,27]	$C_9H_9N_3O_2S_2$	255.31	7.2	373	0.05	
	Sulfadimethoxine [25,27]	$C_{12}H_{14}N_4O_4S$	310.33	5.9	343	1.63	
	Sulfamethazine [25,27]	$C_{12}H_{14}N_4O_2S$	278.33	7.59	1500	0.89	
	Sulfachloropyridazine [25,27]	$C_{10}H_9ClN_4O_2S$	284.72	5.49	7000	0.3	
	Sulfamerazine [25,27]	$C_{11}H_{12}N_4O_2S$	264.30	7.0	202	0.14	
	Sulfamethaxazole [21,25,27,29]	$C_{10}H_{11}N_3O_3S$	253.28	5.6	610	0.89	
	Sulfamethizole	$C_9H_{10}N_4O_2S_2$	270.33		1050	0.54	
Hormones	Estrone [5,29]	$C_{18}H_{22}O_2$	270.37	10.4	30	3.13	
	Progesterone	$C_{21}H_{30}O_2$	314.47		8.81	3.87	
	Testosterone	$C_{19}H_{28}O_2$	288.43		23.4	3.32	
	17α-Ethinylestradiol	$C_{20}H_{24}O_2$	296.41		11.3	3.67	

Table 1 (*Continued*)

Chemicals	Name	Molecular formula	Molecular weight (g/mol)	p*Ka*	Solubility in water (mg/l)	log P_{ow}	Structure
	Estriol	$C_{18}H_{24}O_3$	288.39		441	2.45	
	Estradiol	$C_{18}H_{24}O_2$	272.4	10.4	3.6	4.01	

to these synthetic solutions, 10 ppb antibiotics and hormones were mixed with tap water to analyze the effect of slightly more complex water compositions. Tetracyclines, sulfanamides and selected hormones were used for the experiments. A list of chemicals and their characteristics are given in Table 1. pH of the solutions were adjusted to 7.

3.1. Analytical methods

3.1.1. Antibiotics

Antibiotics were extracted using the method described by Lindsey et al. [25]. Prior to extractions, samples were kept in 250 ml amber glass bottles and stored at −20 °C. Samples were prepared for extraction by adding 100 μl of 40% H_2SO_4, and 0.75 g of disodium ethylenediaminetetraacetate (Na_2EDTA) to the bottle containing 170 ml of permeate or 30 ml of concentrate samples. To achieve dissolution of the Na_2EDTA, the bottles were agitated on an orbital shaker for 60 min at 100 rpm. Antibiotics were extracted using 60-mg HLB (hydrophilic-lipophilic balance) Oasis® brand cartridges from Waters (Millford, MA). Cartridges were preconditioned with 3 ml of MeOH, 3 ml of 0.5N HCl, and 3 ml of distilled water. Samples were then passed through the cartridges at 10 ml/min. After isolation, the cartridges were rinsed with 1 ml of distilled water to remove excess Na_2EDTA. The analytes were eluted into a test tube using 5 ml of MeOH. The effluents were concentrated under a flow of N_2 to a volume of 0.5 ml by evaporation. Then, 0.5 ml water was added to the tube, and the tube was vortexed for 30 s. The resulting mixture was transferred to 2 ml amber autosampler vials. Finally, 20 μl of the internal standard, 2.5 mg/l simatone, was added to each vial.

3.1.2. Hormones

Hormones were extracted using the method described by Lagana et al. [37]. Hormones were isolated onto 200-mg HLB (hydrophilic-lipophilic balance) Oasis® brand cartridge from Waters Inc. (Millford, MA). The cartridges were prewashed sequentially with 10 ml of dichloromethane:methanol (50:50, v/v), 5 ml of methanol and 10 ml of distilled water. Samples were passed through the cartridges at 10 ml/min. Then the cartridges were washed with 10 ml of water. The retained compounds were eluted with 7 ml of a solution of dichloromethane:methanol (50:50, v/v). The extracts were then evaporated to dryness under a gentle nitrogen stream in a thermostatic bath. The residues were redissolved in 200 μl of a 0.1 mg/l internal standard of ^{13}C-Estradiol.

3.1.3. LC/MS/MS analysis

The LC instrument was a 2695 XE separations module (Waters Corp., Milford, MA) equipped with an Xterra MS C_{18} column (150 mm × 2.1 mm i.d., 5 μm) (Waters Corp., Milford, MA) and operated at a temperature of 45 °C; the injection volume was 10 μl. For both antibiotics and hormones the same mobile-phase gradient was used to separate the compounds: The respective compositions of solvents A, B and C were as follows: A, 1% formic acid–methanol (70:30, v/v); B, water, and C, methanol. The solvents were mixed as follows: 0–1 min 50% A, 50% B, 0% C; 1–12 min a linear gradient from the previous settings to 70% A, 0% B, 30% C; 12–30 min from the previous settings to 7% A, 0% B, 93% C; and finally the instrument was returned to starting conditions from 30 to 32 min and then allowed to stabilize for 10 min with 50% A, 50% B. The total run time was 42 min. The flow through the column was set at the rate of 0.25 ml/min. The analytes were detected using atmospheric pressure ionization-tandem mass spectrometry. The instrument was a benchtop triple quadrupole mass spectrometer (Quattro LC from Micromass Ltd., Manchester, UK) operated in electrospray ionization mode. The source parameters were as follows: capillary voltage was set at 3.0 kV and extractor voltage was set at 3 V, respectively; rf lens at 0.1 V; source and desolvation temperatures were 150 and 450 °C. Liquid nitrogen was used to supply the nebulizer and desolvations gas (flow rates were approximately 80 and 600 l/h, respectively). Argon was used as a collision gas to fragment the parent ions; the typical pressure of the collision cell was 2.6×10^{-3} mbar. Both high and low mass resolutions were set at 12.0 for both quadrupoles. Acquisition was done in the multiple-reaction monitoring mode (MRM) in electrospray positive (ES+) mode. The parent and daughter ions used for compound identification and quantitation are listed in Table 2 along with the optimum cone voltages and collision energies settings that were used for each compound. Optimization for each compound was performed by infusion of the standards using a syringe pump (10 μl/min) mixed with the LC effluent (100% A at 0.2 ml/min). The detector was a photomultiplier set at 650 V. Quantitation of the sulfanamide group of antibiotics was performed using internal standard method utilizing simatone; while calculations of tetracyclines' concentrations were based on the method of standard addition described by Lind-

Table 2
Parent and daughter ions used for quantitation of hormones and antibiotics and MS parameters used to produce them

Compound	Parent ion (Da)	Daughter ion (Da)	Retention time (min)	Cone (V)	Collision (eV)
Chlorotetracycline	479	444	10.1	27	22
Tetracycline	445	410	6.1	20	19
Oxytetracycline	461	426	6.6	18	18
Doxcycline	445	428	12.3	21	18
Sulfathiazole	256	156	3.9	20	17
Sulfadimethoxine	311	156	13.0	33	22
Sulfamethazine	279	186	7.3	30	24
Sulfachloropyridazine	285	156	8.8	22	16
Sulfamerazine	265	108	4.9	35	22
Sulfamethaxazole	254	156	9.1	20	16
Sulfamethizole	271	156	6.9	21	19
Simatone	198	124	8.9	26	20
Estrone	271	253	21.9	20	15
Progesterone	315	109	25.6	14	23
Estradiol	255	159	22.1	14	21
^{13}C-Estradiol	258	159	22.1	22	18
Testosterone	289	109	22.6	25	21
17α-Ethinylestradiol	279	133	22.3	24	16
Estriol	271	133	21.9	22	18

sey et al. [25] because of matrix effects. Concentrations for the hormones were calculated by internal standard method using ^{13}C-estradiol.

3.1.4. Extraction recoveries

To determine extraction efficiencies, duplicate distilled water samples were spiked to contain 0.2 and 2.0 μg/l of antibiotics and hormones, and extracted as described above. Our recovery values ranged from 62 to 114% for antibiotics and from 96 to 106% for hormones. These recoveries are comparable to values reported by others [25,37].

3.1.5. Adsorption studies

Adsorption of antibiotics and hormones on the membrane surface was assessed in batch tests without applying a transmembrane pressure. Antibiotics and hormones were prepared at the concentration of 10 ppb as a feed solution for all experiments. The test solutions were mixed at the same stirring speed as that applied in rejection experiments and samples were collected for every 30 min from the filtration cell. The total exposure time was 90 min corresponding to the maximum time required to perform a single batch filtration. For many of the compounds under consideration, this period was not long enough to produce a plateau in concentration that would have indicated that the membrane material had reached equilibrium with the solute (Fig. 1a–c). Had all of the solute initially in solution adsorbed to the membrane, a maximum adsorbed concentration on membrane surface of 6850 ppb/m^2 would be produced.

4. Results and discussion

Retention of solutes by NF membranes can be affected by several factors such as adsorption, charge effect, straining, etc. [28]. Two measures of solute/membrane interaction were followed in this study; namely, the amount of hormones and antibiotics

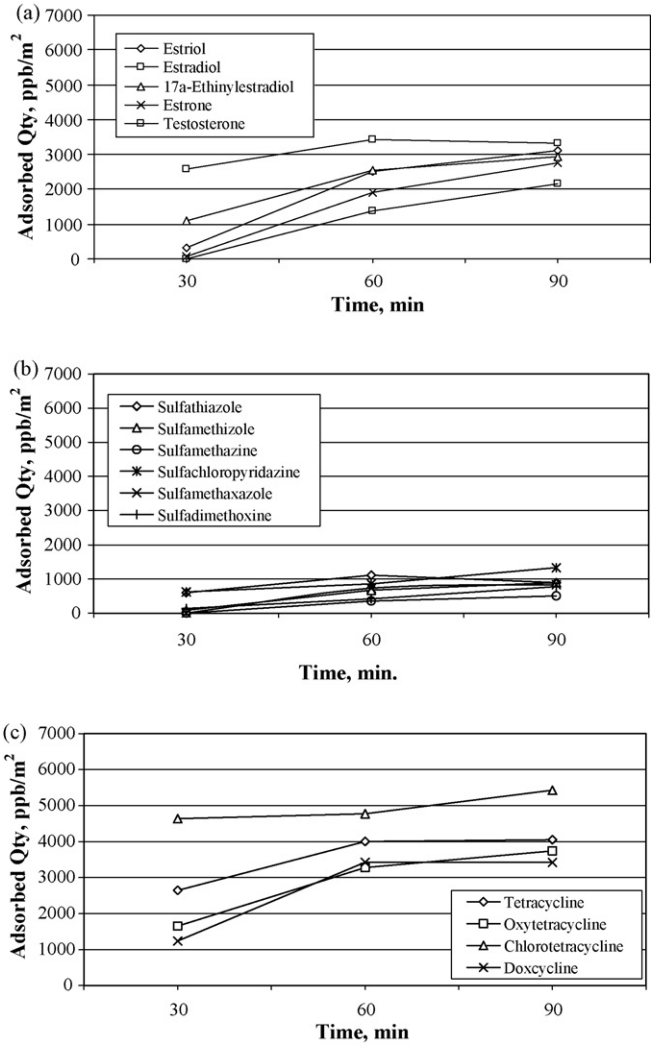


Fig. 1. Adsorbed quantity of hormones and antibiotics on NF membrane without pressure. (a) Hormones, (b) sulfanamides and (c) tetracyclines.

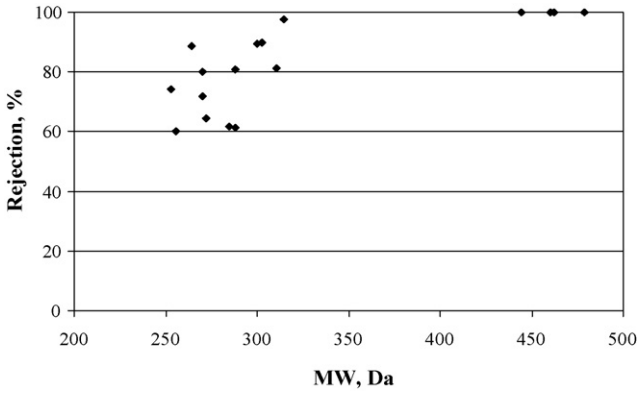


Fig. 2. Rejection vs. molecular weights.

adsorbed on membrane surface and apparent retention/rejection of these compounds across the membrane.

4.1. Adsorption

The highest rate of adsorption was observed for the tetracyclines. Almost 80% of chlorotetracycline was adsorbed on the membrane surface with stirring after 90 min and most of this (nearly 70%) had adsorbed after 30 min (Fig. 1c). In contrast, adsorption of doxcycline on these membranes was much less favored. Between 30 and 60 min, adsorbed doxcycline increased from less than 15% to nearly 50% and remained more or less and unchanged after 90 min. The degree to which hormones adsorbed was lower (between 22 and 46%) than those obtained for the tetracyclines. The sulfanamide antibiotic group showed slow adsorption kinetics and relatively little mass adsorption, rising to only 11–20% after 90 min (Fig. 1b). In most cases, the greatest rates of adsorption appeared to occur between 30 and 60 min after which they were often essentially stabile. In addition to adsorption, other mechanisms such as degradation, volatilization and sorption to walls of test device may also account for losses other than adsorption onto membrane surfaces.

4.2. Overall rejection

The observed values of membrane rejection for all of the chemicals tested are plotted as a function of molecular weight in Fig. 2. Removal efficiencies increased with molecular weight and were higher than 95% after molecular weight of 300 Da. Complete removals were obtained for tetracyclines, which have molecular weights greater than 450 Da. The molecular weight cutoff is approximately 300 Da for the NF200 membrane which can explain the low removal efficiencies at low molecular weights.

4.3. Effect of water matrix

4.3.1. Rejection of hormones

Rejections of hormones present in solutions of variable ionic composition ($CaCl_2$, NaCl, tap water and humic acid) are summarized in Fig. 3 for only estradiol, estrone and testosterone since the other compounds had similar trends. The rejection of hormones introduced to the membranes as solutions in only DI water were quite low in comparison with the rejections observed when virtually any additional solute(s) was present. For example, in a solution of only DI water, the rejections of estradiol and testosterone were 64 and 62%, respectively. The largest rejections observed in DI water solutions were for 17α-ethinylestradiol (90%) and progesterone (98%). When hormones were added in conjunction with tetracyclines and sulfanamides, rejection of hormones increased in all cases to values over 95–98%. Tetracyclines have hydrophobic characteristics and can associate with hormones. This may increase the rejection of hormones if it is mixed with tetracyclines. Similarly, when 10 mM calcium or humic acid (10 mg/l) were added to the feed solution, the rejection of the hormones increased to values of approximately 95% or greater with slightly higher values observed for the hormones alone. These observations of enhanced removal of hormones in the presence of humic acid can be explained by the influence of natural organic matter [38–40]. Hormones can associate with the functional groups present on NOM and form macromolecular complex. This may increase the effect of size exclusion and the adsorption of hormones onto membrane surface [38]. Hormones also can make a complex with calcium and this can also effect the rejection of hormones.

The effect of ionic strength was studied by the addition of 10 mM NaCl to the feed solution. Although, ionic strength can influence the electrostatic interactions between fixed charge groups of organic macromolecules and hence their conformation, its effect on the size and shape of small organic macromolecules is expected to be negligible. However, it may effect the electrostatic interactions between the membrane functional groups and this may result in changes in the effective membrane pore size [41]. As shown in Fig. 3, after addition of NaCl to the hormones solution, hormone rejection was higher than the rejections obtained at zero ionic strength. However, it was slightly lower compared with the rejections observed when calcium, humic acid, and/or the other trace organic compounds (tretracyclines or sulfanamides) were added. The zeta potential of the membrane reduced, as the ionic strength increased, which is in good agreement with the electrical double layer compaction theory. As ionic strength increased, the zeta potential of the polyamide NF200 membrane exhibited more negative values [42]. This may effect the rejection of hormones at high ionic

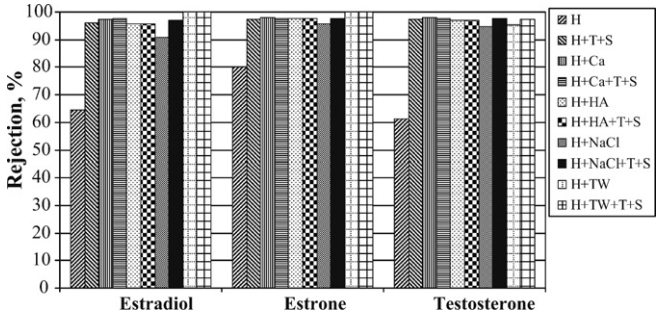


Fig. 3. Hormones rejection at different conditions (H: hormones; T: tetracyclines; S: sulfanamides; Ca: calcium; HA: humic acid; NaCl: sodium chloride; TW: tap water) (H = 10 ppb, T = 10 ppb, S = 10 ppb, Ca^{+2} = 10 mM, HA = 10 mg/l and NaCl = 10 mM).

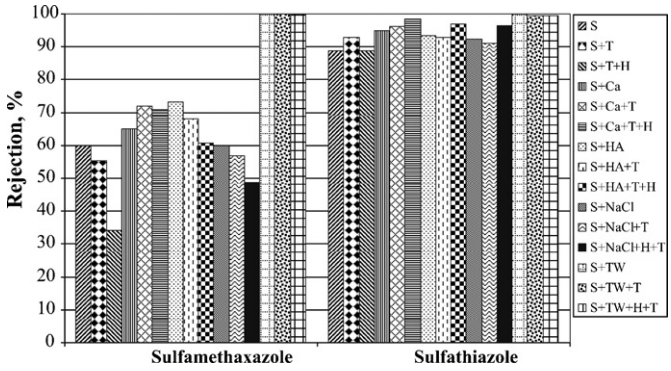


Fig. 4. Sulfanamides rejection at different conditions (H: hormones; T: tetracyclines; S: sulfanamides; Ca: calcium; HA: humic acid; NaCl: sodium chloride; TW: tap water) (H = 10 ppb, T = 10 ppb, S = 10 ppb, Ca^{+2} = 10 mM, HA = 10 mg/l and NaCl = 10 mM).

strength conditions. Rejections of hormones were also studied in tap water. When compared to the other conditions obtained in DI water, the highest hormone rejections were observed with tap water. This may be explained by the influence of both minerals and natural organic matter (NOM) in tap water [37,38,42].

4.3.2. Rejection of sulfanamides

In contrast with the rejections observed for hormones, the rejection of sulfanamides varied greatly with changes in solution chemistry (Fig. 4). The results are given for only sulfamethaxazole and sulfathiazole; however, the others had similar trend. Sulfanamides were typically rejected less than hormones. This may be due in part to the smaller molecular weights of sulfanamides. Sulfamethaxazole had the smallest molecular weight, 253 g/mol and yielded the smallest rejection among the sulfanamides. However, the low rejection of sulfanamides may also be related to the absence of hydroxyl groups on the sulfanamide chemical structures and fact that experiments were performed at pH of 7 where the sulfanamides are largely uncharged. Low rejection of sulfamethaxazole according to sulfathiazole can be because of low pKa value.

The addition of tetracyclines to the sulfanamide solutions had little effect on the rejection of sulfanamides. However, mixture of tetracyclines, sulfanamides and hormones increased slightly the rejections of sulfamerazine, sulfachloropyridazine and sulfadimethoxine. The addition of calcium also slightly increased the sulfanamide rejections. The highest sulfanamide rejections in the calcium experiments were observed for the solution where calcium, sulfanamide, tetracycline, and hormone were mixed together. Similar results were also obtained with the experiments where humic acid was added. Some of the highest rejections were observed for more complex solutions such as those that included tap water. Adams et al. [27] achieved a rejection rate of 90% by reverse osmosis membranes for sulfanamides dissolved in river water which contains natural organic matter, comparable with the results of this study. Tetracyclines have adsorptive characteristics on the membrane surface and could not associate with sulfanamides which resulted small increase of sulfonamide rejection. After an addition of hormones to sulfonamide and tetracycline mixture, hormones and tetracyclines

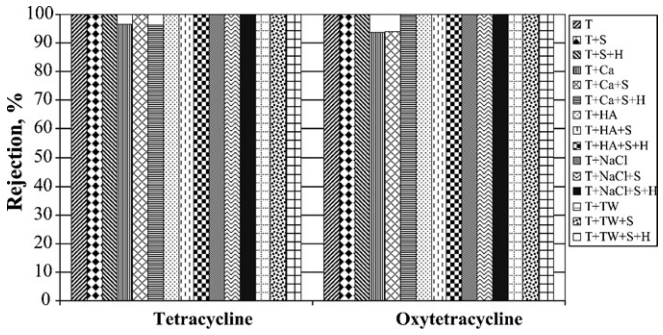


Fig. 5. Tetracyclines rejection at different conditions (H: hormones; T: tetracyclines; S: sulfanamides; Ca: calcium; HA: humic acid; NaCl: sodium chloride; TW: tap water) (H = 10 ppb, T = 10 ppb, S = 10 ppb, Ca^{+2} = 10 mM, HA = 10 mg/l and NaCl = 10 mM).

associated together and sulfanamides became neutral which also decreased the sulfanamide rejection through the NF200 membrane.

The addition of 10 mM NaCl to feed solution had almost no effect on sulfanamide rejection. Rejections were the same as those observed at zero ionic strength. Similar results were observed by Namguk et al. [39] for the hormone mimicking trace organic compounds.

4.3.3. Rejection of tetracyclines

The tetracyclines evaluated were all nearly completely removed (Fig. 5). The results are given for only tetracycline and oxytetracycline, since the others had similar trends. High rejections can be explained because of the high molecular weight of the tetracycline's which were between 444 and 479 g/mol according to molecular weight exclusion range NF200 membrane. There was a slight decline on the rejections of tetracycline's mixed with calcium, similar to result obtained by Devitt et al. [31] in a study of atrazine rejection by NF membranes.

5. Conclusions

The solution chemistry, organic matter and salinity affect the rejection of tetracycline's and sulfanamides and selected hormones by NF membranes. Tetracyclines have a high adsorptive affinity for the membrane while the adsorption rates for hormones are lower. An addition of antibiotics to hormone solution increases the hormone rejections while almost complete rejections were observed for tetracyclines. Not only the humics and other organics but also antibiotics influence the hormone rejection.

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